# AN EVALUATION OF LEATHER PREPARED FROM DEHYDRATED HIDES AND SKINS WHICH HAD BEEN TREATED WITH SELECTED ALKYLENE GLYCOL DERIVATIVES BEFORE DRYING

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## ABSTRACT

Grain split sides after the bating step and fresh calfskins were treated with aqueous solutions of selected alkylene glycol derivatives, air-dried at ambient temperatures, and then sent to various co-operating tanners to be prepared into finished leather. The finished leather was evaluated subjectively by the tanner and returned for further examination and chemical and physical testing. Some of the finished leather was acceptable and some was not. Further study of the dehydration and rehydration steps is needed to explain this variability.

## INTRODUCTION

In previous publications we described a novel process for the dehydration of animal hide products (1, 2). This process involves impregnation of the hide with aqueous solutions of certain alkylene glycol derivatives and then air-drying to give a product with good fiber separation. This product is markedly whiter, more supple, and softer than conventional "flint" dried raw stock, which is stiff, hard, and discolored.

The previous study also indicated that the use of this treated, dehydrated stock for the preparation of chrome-tanned leather did not show any interference with the chrome uptake and its effect on the shrink temperatures of the tanned stock. At this point it was of particular interest to evaluate further the treated, dehydrated stock as a substrate for finished leather. The present report describes experiments on converting into finished leather grain split sides and calfskins that had been treated with selected aqueous alkylene glycol solutions and air-dried.

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## EXPERIMENTAL METHODS AND RESULTS

### Chemical and Physical Tests

The assay for chromic oxide was carried out by following the Official Methods of Analysis of the ALCA, using the alkaline fusion method and titration with sodium thiosulfate (3). The physical tests also followed the above standard methods, with the exception of the SATRA Grain Crack Test. The SATRA Lastometer Mark II† was used according to the method I.U.P. 9 of the Official Methods of the International Union of Leather Chemists Societies, where it is called the Ball Burst Test (3–5). These results are given the following interpretation. A distension at grain crack of 7.0 mm. or over should give a leather which will be satisfactory for lasting in most cases. A result below 6.00 mm. represents a leather which is definitely below standard and unsuitable for lasting.

### Treatment of Grain Splits After the Bating Step

Bated grain splits were the initial substrates selected for treatment and subsequent tannery evaluation of the leathermaking properties of the air-dried product. Three bated sides were received from a local tannery and each side was treated with a 25 percent by weight solution of butyl Carbitol®, $C_4H_9O(C_2H_4O)_2H$, or Carbitol acetate®, $CH_3COO(C_2H_4O)_2C_2H_5$, or Carbowax® 550, $CH_3O-(C_2H_4O)_xH$, respectively. Float levels of 100 percent, based on the weight of the side, were used and will be used for all further treatments, unless other percent float levels are specifically mentioned. The sides were tumbled in a large stainless steel drum at six R.P.M. for 3.5 hours. After treatment, the sides were toggled and allowed to air-dry. The dehydrated hides were white and clean. Two weeks after treatment the sides were sent out for processing into finished leather.

The dehydrated sides which were treated with butyl Carbitol or Carbitol acetate were less plump and less flexible than the side treated with the Carbowax 550. A vein pattern also developed after drying on all the sides. This pattern appeared on both the grain and flesh parts of the sides and the patterns on the grain were generally independent of the patterns on the flesh side. The tanner, however, was not too concerned about these patterns. He reported the sides to be very strong and also remarked that they appeared to wet back nicely. After chrome tanning, the sides exhibited a fine draw pattern on the grain and this caused some concern. However, after fatliquoring and toggling, the sides were mellow, full, and considered satisfactory. In the opinion of the tanner, the leather produced from these sides was too soft for shoe upper leather but was suitable for use as a softie type leather in hand sewns, gloves, bags, or garments.

### Treatment of Freshly Flayed Calfskin

Calfskin from freshly slaughtered animals was selected as the raw stock to be used for evaluating the dehydration process, and butyl Carbitol was selected as

†Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

the treating agent. These skins weighed about 15 to 18 pounds untrimmed. They were obtained at the abattoir soon after slaughter and were packed in ice for transportation back to the Laboratory. Here the skins were trimmed and cleaned of any large pieces of flesh and fat.

A number of experiments were run to determine the leathermaking qualities of the dehydrated, preserved calfskins. In the first experiment, one full skin was treated with a 20 percent by weight solution of butyl Carbitol in a drum tumbled at six R.P.M. for 24 hours. The skin was toggled and air-dried white and clean. This skin was held approximately three months before it was sent to a tannery for processing into finished leather. The tanner remarked that, although it took two days to wet back, it made a good and a strong finished leather. He was particularly interested in the plumpness of this stock.

Physical test data on the leather are presented in Table I. Since we had no comparative data on this tanner's normal production, a comparison was made with data obtained on finished calfskin leather from another tannery. These data are also listed in Table I. The experimental calfskin leather gave higher test values than the commercial leather on all the physical properties which were compared.

## A Matched Side Comparison: Brined Half Skin versus Dehydrated Half Skin

The next experiment was set up to substantiate the previous experimental results obtained using a full calfskin and also to obtain controlled, intraside physical test data. To do this, three freshly flayed calfskins were used in a matched side study in which the experimental controls were a brined matched half calfskin. This technique gives a closer control on the variability of the individual skin, and also the brined stock represents the usual raw material used by the industry. The half calfskin used will be referred to by use of the term half skin rather than side, since the term side is used to refer to a half of a steerhide or cowhide. Three full calfskins were split down the backbone and one half of each skin was brine-cured to be used as a control. The brined skins were prepared by tumbling for 24 hours in a churn containing a saturated salt solution and excess solid salt. After horsing the half skins to drain off excess liquid, additional salt was rubbed over the flesh surface to insure adequate salting. The remaining half skins were tumbled for 24 hours at six R.P.M. in a 20 percent by weight butyl Carbitol solution. These half skins were then toggled and air-dried to give a white and clean substrate. They were held for three weeks before being sent to a tanner for processing into finished leather, which was then evaluated. In this experiment the skins were processed and finished at a different tannery. At this tannery the skin halves received a 24-hour soak and then were treated as normal production. At this time the tanner felt that the skin halves were adequately hydrated. His remarks on the finished leather are as follows. The matched skin half, 1A-a butyl

## TABLE I

COMPARISON OF PHYSICAL DATA ON LEATHER PREPARED FROM A CALFSKIN WHICH WAS TREATED WITH BUTYL CARBITOL AND DEHYDRATED WITH THOSE OF A COMMERCIAL CALFSKIN LEATHER

| Sample | Mullen Grain Crack | | | Tensile | | Tensile & Slit Tear | Slit Tear |
|---|---|---|---|---|---|---|---|
| | Thickness (in.) | Extension (%) | Load to Crack (lbs.) | Elongation (%) | Tensile (P.S.I.) | Direction to Backbone | Tear Strength (lbs.) |
| Commercial Leather | .057 | 36 | 390 | 63 | 3435 | Paral. | 19 |
| | | | | 46 | 4120 | Perp. | 21 |
| Experimental Leather | .059 | 90 | 940 | 57 | 5460 | Paral. | 42 |
| | | | | 58 | 4430 | Perp. | 33 |

Carbitol treated half, showed belly draw and the break was not as good as the matching brine control half, 1B, which appeared to be quite normal. In a comparison of matching skin halves 2A and 2B, the treated and brined side, respectively, both looked approximately the same but the brined half was rated poor for both break and draw. Matched skin halves 3A and 3B, the treated and brined half, respectively, were also rated poor for both draw and break. In summary, only the skin half 1B, which was a brined half, gave an acceptable leather. All the other leather, whether it was prepared from a treated or a brined control skin half, was rated poor on the basis of break or belly draw or both.

Physical tests and chromic oxide content were run on the finished leather to determine the effect, if any, of the treatment on these measured properties when compared to the same data obtained on the control leather. The data are listed in Table II. The chrome content does not appear to be affected by the treatment, as all the chrome values, except for side 1A, compare quite closely. The physical test values show that in all cases, even when the data included matched skin halves with over-all low test values, the treated leathers gave higher results than the control leathers.

The problem with this experimental lot of skins was the poor appearance of the finished leather from both the treated and the brined control skin halves. The tanner felt that this appearance was an indication that the soak period had not been long enough. To check this out, another experiment was conducted with the dehydrated skins receiving a soak period of 48 hours.

## Effect of Longer Rehydration Time and Use of Less Butyl Carbitol

In this experiment it was decided to use as a comparison control an acceptable, representative finished calfskin leather from the tanner's regular production. The opportunity was also taken to gather some information on the effect of using half as much butyl Carbitol as a treatment on the fresh calfskins as had been used in the previous experiments. The matched side technique was used again, with one half of the skin being treated with a 50 percent float of a 20 percent by weight butyl Carbitol solution and the matching side treated with a 100 percent float of 20 percent Carbitol solution. The skin halves were tumbled at six R.P.M. for 24 hours and then were toggled. They air-dried white and clean-looking. The dehydrated half skins were sent to the tanner for an evaluation of their leather-making properties approximately one month after treatment. The tanner rehydrated these skins for 48 hours, which was 24 hours longer than in the previous experiment. The tanner did not make any detailed comment on this lot of calfskin leather. However, it was his opinion that this leather was much more acceptable than the previous lot which had received the shorter soak. In our judgment, the skin halves treated with the lower float made a leather which was comparable in appearance to the leather prepared from matching skin halves treated with the higher float and it all compared favorably to the commercial leather.

## TABLE II

PHYSICAL TEST DATA AND CHROMIC OXIDE CONTENT OF LEATHER PREPARED FROM BUTYL CARBITOL TREATED AND DEHYDRATED CALFSKINS COMPARED TO THOSE OF LEATHER PREPARED FROM BRINED CALFSKINS

| Sample | Mullen Grain Crack | | Satra Grain Crack | | Tensile | | Tensile & Slit Tear | Slit Tear | $Cr_2O_3$ |
|---|---|---|---|---|---|---|---|---|---|
| Identification | Extension (%) | Load to Crack (lbs.) | Extension (mm.) | Load (kg.) | Elongation (%) | Tensile (P.S.I.) | Direction to Backbone | Strength (lbs.) | On Dry Basis (%) |
| 1A* | 60 | 480 | 8.35 | 38 | 43 | 5140 | Paral. | 30 | 5.35 |
| | | | | | 51 | 5280 | Perp. | 23 | |
| 1B* | 53 | 390 | 6.30 | 14 | 36 | 3730 | Paral. | 16 | 4.85 |
| | | | | | 57 | 3540 | Perp. | 17 | |
| 2A | 68 | 570 | 7.33 | 35 | 44 | 5130 | Paral. | 22 | 4.75 |
| | | | | | 63 | 4740 | Perp. | 24 | |
| 2B | 56 | 500 | 7.00 | 29 | 37 | 4590 | Paral. | 15 | 4.84 |
| | | | | | 59 | 4300 | Perp. | 22 | |
| 3A | 43 | 240 | 6.39 | 64 | 49 | 4430 | Paral. | 28 | 4.78 |
| | | | | | 65 | 4635 | Perp. | 17 | |
| 3B | 30 | 160 | 4.58 | 7 | 39 | 2890 | Paral. | 14 | 4.61 |
| | | | | | 40 | 2690 | Perp. | 14 | |

*A and B refer to matching halfskins. All the A halfskins were butyl Carbitol treated and the B halfskins were brine-treated. The halfskins were soaked by the tanner for 24 hours and then treated as normal production.

## TABLE III

### PHYSICAL TEST DATA AND CHROMIC OXIDE CONTENT OF LEATHER PREPARED FROM BUTYL CARBITOL TREATED AND DEHYDRATED CALFSKINS COMPARED TO THOSE OF A COMMERCIAL CALFSKIN LEATHER

| Sample | Mullen Grain Crack | | Satra Grain Crack | | Tensile | | Tensile & Slit Tear | Slit Tear | $Cr_2O_3$ |
|---|---|---|---|---|---|---|---|---|---|
| Identification | Extension (%) | Load to Crack (lbs.) | Extension (mm.) | Load to Crack (kg.) | Elongation (%) | Tensile (P.S.I.) | Direction to Backbone | Tear Strength (lbs.) | On Dry Basis (%) |
| Commercial Calfskin Leather | 36 | 390 | 6.20 | 20 | 63 | 3435 | Paral. | 19 | 5.70 |
| | | | | | 46 | 4120 | Perp. | 21 | |
| 1A* | 57 | 558 | 7.35 | 28 | 43 | 7655 | Paral. | 21 | 6.07 |
| | | | | | 112 | 3715 | Perp. | 27 | |
| 1B* | 54 | 583 | 6.37 | 20 | 48 | 5265 | Paral. | 17 | 6.17 |
| | | | | | 56 | 4000 | Perp. | 24 | |
| 2A | 36 | 322 | 5.75 | 11 | 52 | 4745 | Paral. | 17 | 6.09 |
| | | | | | 68 | 4095 | Perp. | 24 | |
| 2B | 38 | 312 | 6.40 | 17 | 52 | 4595 | Paral. | 17 | 6.02 |
| | | | | | 93 | 2950 | Perp. | 23 | |
| 3A | 71 | 548 | 6.35 | 25 | 43 | 6250 | Paral. | 19 | 6.11 |
| | | | | | 62 | 4840 | Perp. | 24 | |
| 3B | 47 | 630 | 6.51 | 36 | 45 | 6055 | Paral. | 19 | 6.24 |
| | | | | | 67 | 3575 | Perp. | 24 | |

*A and B refer to matching halfskins. All the A halfskins were treated with a 100 percent float of a 20 percent by weight butyl Carbitol solution and the B halfskins were treated with a 50 percent float.

The physical test data and the chromic oxide contents of these leathers are presented in Table III. The chromic oxide content of the experimental leather is slightly higher than that of the commercial leather but generally the data in Table III indicated that the lower treatment level gave a leather which was comparable to that produced by the higher level of treatment and that the experimental leather was comparable to the commercial leather. This experiment also indicated that an inadequate rehydration time was probably the reason for the poor appearance of the leather produced in the previous experiment.

## CONCLUSIONS

It was possible to prepare commercially acceptable leather from grain split sides which had been treated after the bating step with aqueous solutions of either butyl Carbitol, Carbitol acetate, or Carbowax 550 and then air-dried.

The evaluation of the experimental leather prepared from the freshly flayed calfskin which had been treated with an aqueous butyl Carbitol solution and then air-dried gave variable results. In the judgment of the tanners, some of this leather was acceptable and some was not. The experimental data and communications from the people who worked with this treated, dehydrated stock indicate that more study is needed on the dehydration process or rehydration method so that adequate rehydration is effected and consistently acceptable leather can be produced.

A limited matched side study on the dehydrated, treated calfskins indicated that the float could be reduced from 100 percent of a 20 percent by weight butyl Carbitol solution to a 50 percent float and still give a comparable leather. The experimental leathers produced from the butyl Carbitol treated, air-dried calfskins were generally equal to or better than the comparison control leathers, when judged on the basis of physical test data.

## ACKNOWLEDGMENTS

The authors wish to thank Mr. William Palm, Mr. George Riser, and Dr. Joseph Naghski of our Laboratory for technical assistance and to acknowledge the co-operation of Barrett and Company, A. C. Lawrence Leather Company, Swoboda and Sons, and Pechin and Fensler and various members of their staff. Bill Fensler (deceased) will be particularly missed because of his boundless enthusiasm and most valuable assistance.

## REFERENCES

1. Hopkins, W. J., Luvisi, F. P., and Filachione, E. M. *JALCA*, **66**, 52–9 (1971).
2. Hopkins, W. J., Luvisi, F. P., and Filachione, E. M. U. S. Patent 3,292,271 (December 20, 1966).

3. Official Method of Analysis, ALCA (1957). May be secured from the Secretary-Treasurer of the ALCA, Tanners' Council Research Laboratory, University of Cincinnati, Cincinnati, Ohio 45221.
4. Measurement of Distension and Strength of Grain by the Ball Burst Test. *J. Soc. Leather Trades' Chemists,* **44**, 371 (1960).
5. Official Methods. *J. Soc. Leather Trades' Chemists,* **45**, 375 (1961).

Received December 8, 1970.